

Titrimetric Monitoring Of Anaerobic Digestion: VFA, Alkalinities and More

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Abstract Volatile fatty acids and bicarbonate measurements are important to assess a digester's stability and to control it. Titration methods are the most likely cost-effective methods to determine those variables with acceptable accuracy. In this paper, titrimetric methods will be classified and evaluated. Two titrimetric sensors are compared for their potential on-line use. One sensor uses advanced interpretation techniques to quantify almost any buffering system while the other uses approximate methods that assume bicarbonate and VFA are the dominating buffers. A specific experiment was performed to run the two sensors during an overload situation of a 1 m³ fixed bed anaerobic reactor with the aim to assess their accuracy. Also, the results show the dynamic evolution of bicarbonate and VFA in the digester during overload conditions. In addition to VFA and bicarbonate, lactate was determined titrimetrically during the overload conditions.

Keywords Alkalinity; anaerobic digestion; lactate; on-line titrimetric sensor; overload; VFA

Introduction

It is generally accepted that alkalinity is very important to assess the anaerobic digestion stability. The main alkalinity components in a digester are bicarbonate and VFA which are consumed and produced through the process steps. Bicarbonate buffers the system in the optimum pH range for the process to run efficiently. VFA buffers the system at low pH that is inhibitory to the biomass matrix in the digester. Bicarbonate is maintained by CO₂ production in the digester. The anaerobic digestion consists of a train of biological activities. With simplification they are, in order, acidogenesis, acetogenesis and methanogenesis. Both CO₂ and VFA are produced first, in addition to H₂, by acidogenesis and acetogenesis. Successively, methanogenesis occurs in two forms. Acetotrophic methanogenesis utilises VFA in the form of acetate only and produces methane and CO₂. Hydrogenotrophic methanogenesis utilises CO₂ and H₂ for the production of CH₄. The bottleneck here is that methanogenic bacteria are more delicate compared to acidogenesis and acetogenesis. Therefore, during toxic events they are more inhibited and during organic overload they cannot catch up with the previous steps. Consequently, VFA starts to accumulate while CO₂ is continuously stripped to the gas phase, pH decreases, biological activities are inhibited and the digester stops functioning. An additional effect is the mutual relation between both forms of methanogenesis. For instance, if the hydrogenotrophic form is inhibited, H₂ will start to build up to a level that inhibits acetogenesis and therefore less acetate becomes available for the other form. VFA's as well as lactate will start to build up in the reactor (Bjornsson *et al.*, 2001).

Titrimetric methods are found to be the most cost effective analysis for VFA and alkalinity with acceptable accuracy (Buchauer, 1998; Vanrolleghem and Lee, 2003). Therefore, many titrimetric methods were developed to determine VFA and alkalinity to study and control the overload conditions and evaluate the impact of toxicities. Moreover, lactate can be measured by

titration and hence can be used as a direct indicator of overloads as will be shown in this paper. Due to the large number of titrimetric methods developed so far, their common basis will be highlighted here. They will be classified into general categories according their interpretation methods. The factors influencing their accuracy will be highlighted through the comparison of two titrimetric sensors in monitoring a digester under overload conditions.

Methods

Titrimetric methods: general basis

Titrimetric methods have the same basis taken from equilibrium chemistry. From the equilibrium of a buffering system (weak acid / weak base), mass balances and the water dissociation reaction, the buffer ions can be defined in terms of total concentration. Examples for acetate (monoprotic) and bicarbonate (diprotic buffers) are given in equations (1) and (2):

$$Ac^- = \frac{K_{ac}}{H^+ + K_{ac}} \cdot Ac_T = f_{Ac^-}(K_{ac}, H^+) \cdot Ac_T \quad (1)$$

$$HCO_3^- = \frac{1}{1 + \frac{K_{C2}}{H^+} + \frac{H^+}{K_{C1}}} \cdot C_T = f_{HCO_3^-}(K_{C1}, K_{C2}, H^+) \cdot C_T \quad (2)$$

Similarly, ions from triprotic buffers can be presented as functions of their total concentration. After addition of a titrand (e.g. strong acid) to a sample the concentration of acid in the sample will be C_a and the concentration of H^+ will shift to mention the charge balance in equation (3).

$$C_a = H^+ + Z - \sum_{i=1}^n z_i \cdot f_{A_i}(\{K_{A_i, p=1 \rightarrow z_i}\}, H^+) \cdot A_{i_T} - \frac{K_w}{H^+} \quad (3)$$

Z is the total alkalinity and z_i is the ion charge. equation (3) forms the general basis of titrimetric methods and the only difference will be in the further mathematical manipulation and algebraic solution algorithms.

Titrimetric methods: classification

From the mathematical point of view the titrimetric methods can be classified into 3 categories:

Solution of linear algebraic equations. examples of methods under this category are method according to (Moosbrugger et al.1992; 1993) and its extended version by (Lahav et. al., 2002). Presenting equation (3) in terms of mass, results in equation (4):

$$V_a \cdot N_a = (V_a + V_s) \cdot H^+ + V_s \cdot \left(Z - \sum_{i=1}^n z_i \cdot f_{A_i}(\{K_{A_i, p=1 \rightarrow z_i}\}, H^+) \cdot A_{i_T} \right) - (V_a + V_s) \cdot \frac{K_w}{H^+} \quad (4)$$

At each point with a recorded added acid volume and pH, an equation linear in total concentrations can be produced. The equation is not linear in the acidity constants. Assuming values of acidity constants, $n+1$ data points are needed to determine the concentration of n buffers and the total alkalinity. More points can be used to introduce new equations and estimate the error in the results that is mainly due to the assumption of the acidity constants. Iteration over all equations can then be used to reduce the error. To avoid singularity of the produced set of equations, It is necessary to carefully locate the data points. For feasible and accurate solutions, the considered buffers should have sufficiently different pKa values and the data points should be distributed evenly around the pKa values.

Linear regression. A good example of this approach is the method of (Kapp, 1984; 1992). The method uses the regression model in (5). The volume of the acid that causes the change of the pH between two points around the pKa of VFA (e.g. pH₃= 5 to pH₄= 4) is assumed to correspond to VFA concentration. A similar assumption can be made for bicarbonate with good choice of pH₁ and pH₂.

$$VFA = a \cdot (V_{a, pH_4} - V_{a, pH_3}) - b(V_{a, pH_2} - V_{a, pH_1}) + c \quad (5)$$

In fact, using a symbolic derivation, equation (5) can be derived from equation (4). The

derivation was made using the Matlab symbolic toolbox assuming that the carbon system is mainly due to the bicarbonate buffer and it was found that:

$$a = f_1(k_{ac}, k_{HCO_3}, N_a, V_s, pH_1, pH_2, pH_3, pH_4) \quad (6)$$

$$b = f_2(k_{ac}, k_{HCO_3}, N_a, V_s, pH_1, pH_2, pH_3, pH_4) \quad (7)$$

$$c = f_3(k_{ac}, k_{HCO_3}, Z, N_a, V_s, pH_1, pH_2, pH_3, pH_4) \quad (8)$$

from (6), (7) and (8) it can be seen that defining the regression model is in fact defining 3 combinations of the acidity constants and total alkalinity. The values of the regression model constants a , b and c are dependent on the experiment parameters (volume of sample V_s and normality of titrand N_a), acidity constants and the choice of the pH points. An equation similar to (5) can be produced to determine bicarbonate.

Nonlinear fitting. The model can be presented by equation (3) and directly fitted to the titration data to estimate its parameters. However, for better practical identifiability, a general buffer capacity model can be obtained by equation (3) with respect to pH. The detailed model and the derivation can be found in (Van Vooren, 2000). The model can be presented in simplified form as equation (9). In addition to the important physical meaning of buffer capacity, deriving equation (3) into equation (9) leads to another advantage. The dynamics of the titration experiment are more pronounced and hence better practical identifiability of the acidity constants as well as total concentrations is achieved. Dynamics will be more distinct since g_{A_i} functions in equation (9) compared to f_{A_i} in equation (3) will be of higher order in H^+ and the acidity constants K_{A_i} . Since more parameters are estimated in this advanced interpretation method, more measurement points are required during the titration. Note that the buffer capacity model is still linear in the concentration.

$$\beta = -\frac{dCa}{dpH} = 2.303H^+ \left(\frac{1}{\gamma H^+} + \sum_{i=1}^n g_{A_i} (\{K_{A_i, p=1 \rightarrow k_i}\}, H^+) \cdot A_{i_T} \right) \quad (9)$$

Sensors

Two sensors are used in this study. First, a Titrimetric Sensor, TS (Bouvier et al., 2002) is designed to use approximate interpretation methods of the first two categories, e.g. (Kapp, 1984; 1992; Moosbrugger *et al.* 1992). Second, a Buffer Capacity Sensor, BCS, is using the method of the third category in addition to automatic model building (Van De Steene et al., 2002) and automatic initialisation modules. The automatic initialisation module determines the most probable initial buffer model and estimates bounds on its parameters for robust optimisation. The automatic model building of BCS starts with calibrating the initial model. The residuals (differences between model and data) are analysed and used to suggest a candidate model extension, if needed, i.e. adding an additional buffer with unknown pKa and concentration. Then another fitting cycle is performed with the extended model, the residuals are analysed, a new extension is defined, and so on, until one of the stop criteria is reached. The stop criteria are based on a set of model selection techniques, which determine the optimum BC model and, therefore, pKa's and concentrations of the significant buffers. Also, based on the fitting results a standard deviation is estimated for each of the pKa and concentration values.

The TS is automated to run titration in 3 minutes to capture all the experiment dynamics. The BCS is running a 30 minutes titration to obtain a more detailed titration curve and therefore leads to a lower sampling frequency. Titration was performed by both sensors by addition of 0.1N hydrochloric acid starting from the pH of the reactor that was controlled at pH around 7 to a pH 3.5 for TS and to pH 2.5 for BCS.

Overload experiment

The experiment was designed so that a fixed bed reactor treating vinasses (Steyer et al., 2002) was overloaded in two steps by increasing the flow rate to 5 times the normal flow and later doubling the influent concentration. Consequently, buffer concentrations in the reactor changed 5 and later 10 times, so that the accuracy of the two sensors and their methods could be compared on an extended range of concentrations. Parallel off-line analyses were performed to determine VFA using gas chromatography GC and alkalinity using the standard end point

method.

Lab experiment

During the overload experiment, low concentrations of lactate were detected by the BCS immediately after the start of the overload. Additional lab experiment was performed to test the robustness of the BCS in detecting lactate over a wider range of VFA and lactate combinations and hence to test the effect of the lactate pKa value (3.86) being close to the pKa of VFA (4.7).

Results and discussions

Figure 1 shows the buffer capacity profile measured by the BCS during the experiment. As the overload proceeds, as shown figure 2, the main buffer in the system shifts from the bicarbonate ($pK_a \approx 6.35$) to the VFA ($pK_a \approx 4.75$) buffer plus small concentrations of the lactate buffer ($pK_a \approx 3.86$). Clearly, this is very useful information to detect an overload and the accumulation of VFAs. Indeed, the experiment dynamics provided good conditions to test the sensors over a full range of variation of the two main buffers. It can be noticed from figure 1 that the initial pH of the titrated sample is very close to pH 7. The reactor pH was controlled around this point by continuous addition of NaOH. In such situation pH measurements cannot be used as indicator for the overload (Almeida *et al.*, 2001) but the amount of base added can.

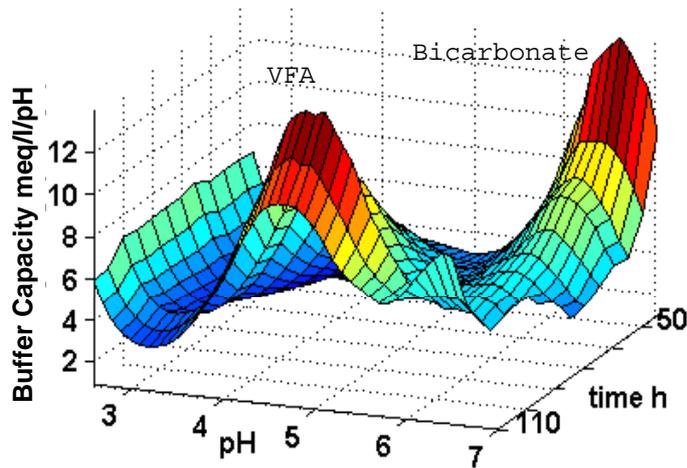


Figure 1: Buffers evolution from bicarbonate alkalinity to VFA during overload

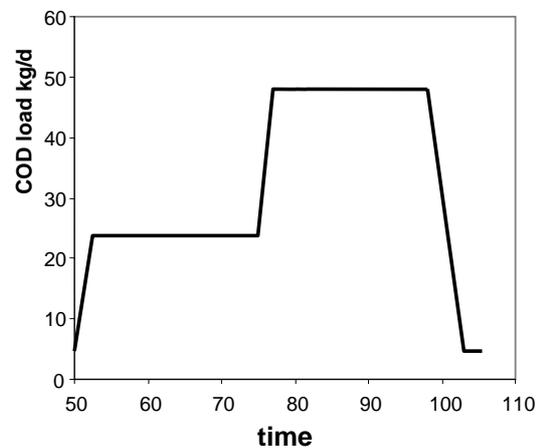


Figure 2: Organic overload to the reactor

Figure 3 shows VFA results from the TS and the BCS compared to the GC and the lactate concentration detected by the BCS. BCS was only tested until 105h. No lactate was detected after the release of the overload at 100h. Figure 4 shows the bicarbonate concentration from both TS and BCS compared to partial alkalinity from the TS and manual end point analysis. For VFA (BCS), the correlation coefficient with GC is $r = 0.977$. For TS $r = 0.758$ but $r = 0.995$ for $VFA < 0.05 \text{ mol/l} \approx 3000 \text{ mg/l}$. The total ionic strength increased due to the higher concentrations and the extra addition of cations (i.e. NaOH) to the reactor. Accordingly, the acidity constants will shift from the original values that were valid during the calibration of the regression model. The regression model constants are functions of the acidity constants, see equations (6), (7), (8). Similar effects will be detected if a method of the first category e.g. (Moosbrugger *et al.* 1992; 1993) is used without correcting the acidity constants. For a method of the third category (e.g. BCS) the accuracy will not be affected since the acidity constants are optimised. Temperature change will also shift the acidity constants and affect the accuracy of the estimated concentrations if the acidity constants are not estimated at the same time. A drift in the pH probe used in the titration analyser will also not affect the results of the BCS approach.

During the overload from 50h to 100h, it can be seen that the partial alkalinity and bicarbonate

are decreasing indicating the overload condition. At 100h the operating conditions were brought to normal and therefore rapid increase of bicarbonate and decrease of VFA occurred. This rapid recovery is related to the design of the reactor which is a fixed bed. In other reactor configurations recovery would be much slower. Partial alkalinity is determined at an end point of 5.75 and therefore, it almost avoids the VFA buffer. Bicarbonate from the TS is determined by a regression model similar to that determined for VFA.

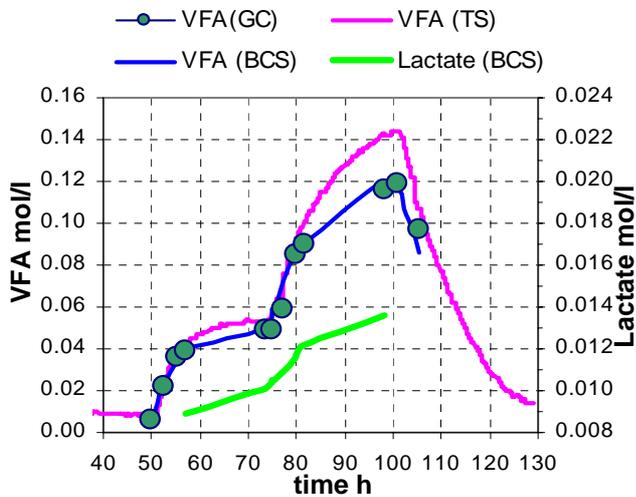


Figure 3: VFA and lactate measurement

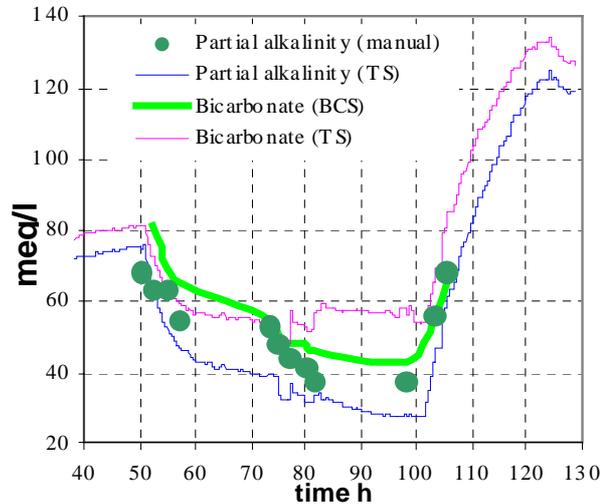


Figure 4: Bicarbonate and partial alkalinity measurement

Outside the overload period, the partial alkalinity and bicarbonate measurements are very close and nicely correlated. During the overload, however, the gap between different measurements increases as the overload proceeds. The shift of the acidity constants increases the influence of the accumulated VFA on the bicarbonate measurement. Recalibration of the regression model for the bicarbonate determination is required for better accuracy during this period. The bicarbonate measurement from the BCS is not influenced by VFA since the acidity constants are optimised for each measurement. The BCS bicarbonate measurement correlates nicely to the partial alkalinity and it is expected to have better accuracy.

In addition to these common factors of shifting the acidity constants, other buffers can affect the accuracy if they are not considered in the calculation procedure or the initial model. For instance, during the overload to the digester in addition to the increase of VFA lactate may be formed and therefore can be a good indicator to the overload and an additional component for advanced understanding of the process behaviour. However, it is not considered in the regression model of the Kapp method and it is therefore quantified by TS as extra VFA. With all methods, if lactate is considered in the calculation procedure or initial model and it is not present in the titrated sample, it is likely that some of the VFA is reported as lactate. Lactate pKa is relatively close to VFA and it may therefore be highly correlated with it. Therefore, in addition to model optimisation, advanced techniques of initialisation and model selection implemented in the BCS will be necessary for the accurate detection of such interfering buffers.

For instance, figure 5 shows a BCS analysis when lactic acid is introduced to the system. the simulated BC curve has two peaks at pH 6.35 and 4.3, they corresponds to the inflection points in the titration curve. Direct interpretation of the curves would lead to the misinterpretation of VFA with considerable shift to pH 4.3. The initialisation module for the BCS will recognise that the second peak is due to (highly correlated) two adjacent buffers. Therefore, it initialises the monoprotic model of lactic acid as well as the bicarbonate and VFA models. Bicarbonate, VFA and lactic acid are then combined in one model that is optimised to get the best fit to the data. The combined model is then tested for possible extension for any further enhancement in fitting the data. In this case, no extension is possible. The optimised and combined model is selected as

the final model. The corresponding pKa's and concentrations of the buffering components are accurately estimated.

The lactate concentration detected by the BCS during the overload experiment previously described was usually less than one tenth of the VFA concentration. An additional lab experiment was thus performed to test wider range of VFA and lactate combinations. The results are shown in figure 6. BCS shows an acceptable accuracy for both VFA and lactate concentrations despite the high correlation and the variation of their concentration ratio. Note finally that, from the same titration experiment, the BCS can also find, next to VFA and alkalinity, other buffers which are important in anaerobic digestion (e.g. ammonia, phenol, phosphorus, hydrogen sulphide...etc.).

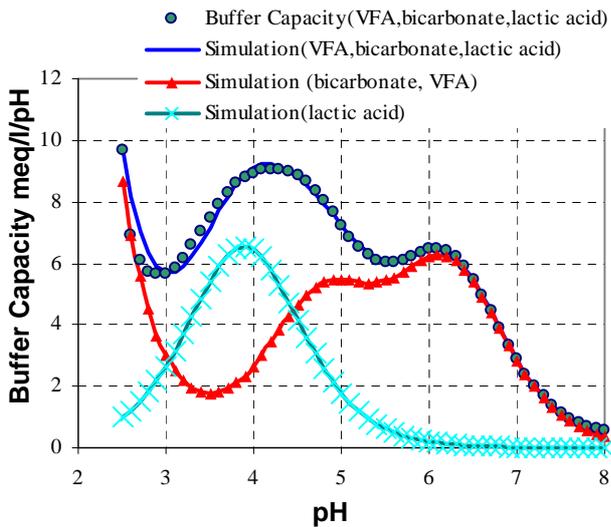


Figure 5: BCS analysis of a simulated bicarbonate, VFA and lactate mixture

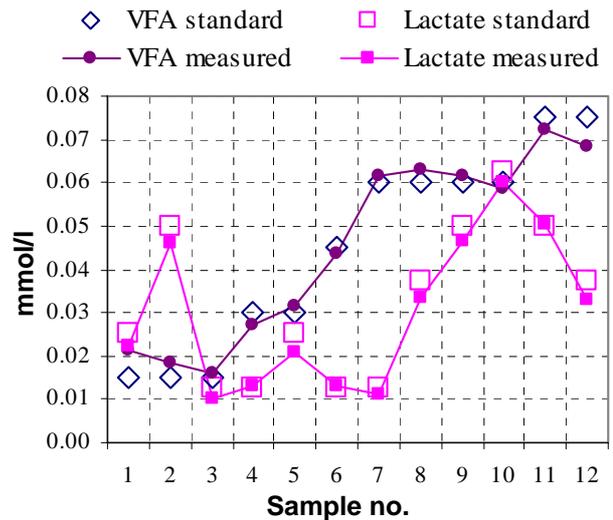


Figure 6: Measuring over a wider range of VFA and lactate combinations

Conclusion

Generally, both the Titrimetric Sensor and the Buffer Capacity Sensor presented here and their interpretation methods (approximate and advanced) show acceptable accuracy for VFA and alkalinity analysis for a large range of operating conditions of a digester and can be used in closed loop control schemes. Added values of the BCS are the accurate results at high concentrations and estimation of other interfering buffers if they exist. Better accuracy is related to the simultaneous estimation of acidity constants. The acidity constants tend to shift due to several factors e.g. temperature and ionic strength or pH meter drift. In the approximate methods acidity constants are either assumed to previously known values e.g. values at standard conditions or estimated in combination via fitting a regression model under certain conditions. To maintain a high accuracy level with the approximate methods, determination of the acidity constants or recalibration of the regression model is essential in case of major changes in the operation conditions. In overload situations to a digester VFAs of higher molecular weight than acetate tend to accumulate. Also, lactate formation is expected. Lactate will decrease the accuracy of VFA determination by the approximate methods. In situations other than treatment of vinasses (used in this experiment), buffer components other than bicarbonate and VFA are likely to exist. These additional buffers are interfering with bicarbonate and VFA (e.g. phosphorus, H_2S and other weak acids) and they should be quantified and considered in the calculation procedure of the approximate methods. This may call for other techniques for measuring these components.

Thus, the BCS can be considered to be a good monitoring tool for anaerobic digestion not only during normal operating conditions but also during overload and exposure to buffering interferences. For determination of this larger set of parameters, a detailed titration curve and therefore good titration hardware is needed. This is feasible on-line with the current

advancement in instrumentation technology , e.g. AnaSense[®] (De Neve *et al.*, 2004). Also its advanced calculations require better computation hardware but a standard PC suffices.

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